On the Isotopic Constitution of Potassium

INAUGURAL DISSERTATION

BY

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This dissertation is based on investigations published in three papers the titles and contents of which follow.

I. The isotopic abundance of ^{40}K. *Arkiv Fysik*, *4*, 203–205 (1951).

II. A direct-coupled amplifier and ratiometer for a single-beam mass spectrometer. *Arkiv Fysik*, *10*, 501–524 (1956).

I. Introduction *501*.

II. The amplifier. 1. The input circuit *503*. 2. The input amplifier stage *504*. 3. The voltage amplifier *508*. 4. The feedback loop *509*. 5. The output circuit *510*. 6. Connections for measurement and calibration *511*.

III. The peak height ratio meter. 1. General *513*. 2. The basic principles of the ratiometer *513*. 3. The design of the ratiometer *514*. 4. The operation of the ratiometer *516*. 5. Sensitivity of the peak height ratio measuring equipment *517*. 6. General remarks on the merits of the ratiometer *521*. 7. Peak height comparator *522*.

IV. Concluding remarks *522*.

III. On the isotopic constitution of potassium. A study of mass discrimination in a hot anode ion source. *Arkiv Fysik*, *11*, 1–54 (1956).

I. Introduction. 1. Problems in determination of absolute isotopic abundance ratio *2*. The isotope ratios in potassium *3*. 3. The method of calibration by synthetic samples *4*. 4. Surface-ionization ion sources *5*. 5. The scope of the present work *7*.

II. The apparatus. 1. Geometry of the magnetic analyser *8*. 2. Mechanical construction of the mass spectrometer *9*. 3. Electrical equipment *12*. 4. Vacuum pumps and gauges *14*. 5. The ion accelerating voltage supply *15*. 6. The ion-source filament current supply *18*. 7. The mass-sweep and chart-drive operating unit *22*. 8. Calibration of the isotope-current measuring equipment *24*.

III. Instrumental errors. 1. Introductory remarks *25*. 2. Erratic mass discrimination of ion source *26*. 3. Influence of beam direction *28*. 4. Collector efficiency *30*. 5. Defocusing effects *31*. 6. Survey of corrections and limits of error *32*.

IV. Measurements of the initial ratio, $^{39}K/^{41}K$. 1. Powdered leucite on filament *33*. 2. Phosphate solutions on filament *34*. 3. Solutions of natural samples *35*. 4. Experiments with the atomic-beam ion source *37*.

V. Measurement of the integral ratio, $^{39}K/^{41}K$. 1. Theory of fractionating evaporation *39*. 2. Atomic beam and indirectly heated anode *39*. 3. Potassium phosphate on filamentary anode *41*. 4. Discussion of the results on the integral ratio *42*. 5. Evaluation of the ratio, $^{39}K/^{41}K$ *45*.

VI. Measurement of the ratio, $^{33}K/^{40}K$. 1. Introductory remarks *46*. 2. Procedure of measurement, and results *47*.

Appendices. 1. Space-charge corrections to peak-ratio measurement *49*. 2. Correction to integral ratio measured, due to incomplete ionization *51*.

Summary

(1) Measurements of the relative abundances of the potassium isotopes exhibit a remarkably large spread, considering that the element is easily ionized and has a molecular weight in the medium range—for which reasons, mass spectra of good resolution and purity are obtained without difficulty. Early mass spectrometric determinations of the ratio $^{39}K/^{41}K$ by electrometric methods gave rather consistent values (Brewer & Kueck[1] 13.88; Nier[2] 13.96) with ion sources and spectrometers of quite different types. The agreement may have been fortuitious, however, since the accidental error limits were rather wide. In later investigations performed with higher accuracy, different observers have arrived at results which are inconsistent—with respect to the stated error limits, mostly less than 1 per cent—when comparing measurements with ion sources of electron-impact type amongst themselves (Paul & Pahl[3] 13.96; White & Cameron[4] 13.66; Nier[5] 13.48), and, likewise, when comparing these with measurements with hot-anode ion sources (Brewer[6] 14.20; Cook[7] 14.12). This state of things emphasizes the question of the systematic errors in mass spectroscopic abundance determination; namely, on one hand, the instrumental errors proper, on the other, the discrimination in the emission of the ion source. All these errors, in so far as they depend on ion mass, are eliminated by calibrating the instrument with synthetic isotope mixtures. The only such attempt made until now,[5] cannot be considered as definitive regarding the potassium isotopes, since the calibration was performed with argon isotopes. (III, Ch. I.)

Also, concerning the ratio $^{39}K/^{40}K$, there exists rather divergent results of measurement (Nier[2] 8600; Brewer[8] 8300; Nier[5] 7800), which are subject to systematic errors of the same kind. The difficulty of obtaining accurate measurements on an isotope of such low abundance as that of ^{40}K, however, results in rather wide limits of accidental measuring errors. (I.)

(2) The abundance of ^{40}K was measured anew with simultaneous measurement of the ratio $^{39}K/^{41}K$. The latter measurement constitutes a calibration of the mass spectrometer with regard to the mass discrimination if the value of the ratio $^{39}K/^{41}K$ is known. If the published ratios $^{39}K/^{40}K$ are reduced to values corresponding to a given ratio, $^{39}K/^{41}K \approx 13.5$, the differences between different determinations are diminished (I). The result of the new investigation can be summarized in the following formula (III, Ch. VI):

$$^{39}K/^{40}K = 7935 \pm 15 + 280\,(^{39}K/^{41}K - 13.57).$$

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[1] *Phys. Rev.*, *46*, 894, 1934.
[2] *Phys. Rev.*, *48*, 283, 1935.
[3] *Naturwiss.*, *32*, 228, 1944.
[4] *Phys. Rev.*, *74*, 991, 1948.
[5] *Phys. Rev.*, *77*, 789, 1950.
[6] *J. Am. Chem. Soc.*, *58*, 370, 1936.
[7] *Phys. Rev.*, *64*, 278, 1943.
[8] *Phys. Rev.*, *48*, 640, 1935.

(3) It seemed as if the disagreement among different types of ion sources were caused by the discrimination in the emission from the hot-anode ion source, notwithstanding that the previous investigation of this factor[9] had given a negative result. Different kinds of surface-ionization ion sources were thus studied, and, in fact, rather large deviations in the ratio $^{39}K/^{41}K$ were obtained under certain conditions. Depending on the structure and depth of the surface coating (mineral powder, evaporation residue of salt solutions), values ranging from 13.9 to 14.2 were obtained in the emission from fresh preparations. Such variations are not incompatible with current conceptions of the emission from ionic crystals. The emission must be largely dependent on the mechanism of transport (diffusion, electrophoresis) within the solids. Generally, a mobility proportional to $M^{-\frac{1}{2}}$ has been considered for isotopes (M = ion mass), but a smaller mass dependence is possible in transport by grain boundaries (as demonstrated experimentally by Chemla & Sue[10]) and through the lattice by aid of vacancies, or in consequence of coupling of the motions of isotopic ions. The value 13.9, therefore, could be regarded as being free from mass discrimination, while the value 14.2 should indicate completely free diffusion with a discrimination ratio amounting to $(41/39)^{\frac{1}{2}}$.

The picture is, however, severely complicated by the fact that extended measurements on very thin coatings (some 1000 monolayers) show a marked fractionation, equivalent to a discrimination factor of $(41/39)^{\frac{1}{2}}$ and an integral value of the ratio $^{39}K/^{41}K$ equal to 13.57; the corresponding result for a 100 times thicker coating being 13.94. This difference is difficult to explain, since a selective loss of sample is not likely to have occurred in the thin preparations to a greater extent than in the thick ones. There is some indication that the measurement of the temporal variations of the isotope ratio in the emission from the thick coatings could not be followed accurately by measurement, and that the average obtained is too high; but it remains doubtful, however, that this error can bridge the gap between the results on coatings of different depths.

Since the more recent determinations of the ratio $^{39}K/^{41}K$ by electron-impact ion sources favour a value below 13.7, there is some support for the result of the present measurements on very thin anode coatings, 13.57 ± 9 (p.e.). This would also make the extremely low ratios (12.6—13.5) found by Brewer[11] in some samples from plants (esp. Pacific kelps), easier to explain. There remains, however, the necessity of finding the cause of the strong discrimination active in the emission from very thick coatings of mineral powders or melts (the hot anode of Brewer and Cook). It is proposed that two selective processes may be cascaded, namely, the diffusion within the solid, and the emission from the surface. In order that the fractionation

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[9] Brewer, *J. Chem. Phys.*, *4*, 350, 1936.

[10] *C. r.* (*Paris*), *236*, 2397, 1953.

[11] *J. Am. Chem. Soc.*, *58*, 365, 1936.

be increased in this way, the main part of the current of matter must be diverted from emission, presumably by transport in the grain boundaries in connection with crystal growth in certain directions where emission is more difficult. During extended measurements on such coatings, very large changes of the isotope ratio are encountered. (III, Sect. V.4.)

If the low value of the ratio $^{39}K/^{41}K$ here adopted, with support of the results of Nier[5] and White & Cameron,[4] is confirmed (e.g. by calibrating the spectrometer with the aid of enriched isotope ^{41}K),[12] then the disagreements mentioned should lead to a more detailed study of the diffusion of isotopes in ionic crystals of different structures. On this subject, there apparently exist no investigations.

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[12] This point was left unsettled, since the experimental work had to be discontinued, owing to external circumstances.